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(54) FORMATION OF WATER-REPELLENT THIN FILM

(57)Abstract:

PURPOSE: To form a highly water-repellent thin film on various substrates with the angle of contact to water controlled to ≥110°C.

CONSTITUTION: Water, solvent, hydrolysis catalyst, silicon alkoxide and fluorine- contg. alkoxide are used as starting chemicals, and the water-repellent thin film is formed on a glass substrate by the sol-gel method. That is, 2-Butanol, ethylene glycol, water and hydrochloric acid are charged, agitated at room temp. and homogenized. The soln. is agitated, orthoethylsilicate is added little by little, and the soln. is agitated at room temp. for one hour. The soln. is allowed to stand for one day to obtain a coating soln. Various substrates are dipped, then pulled up, heated at 100°C for one hour, kept at 160°C for ten minutes, heated at 200°C for one hour and heat-treated at the firing temp. of 400°C for 10-60 minutes to form a thin film.

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CLAIMS

[Claim(s)]
[Claim 1] The method of producing the water-repellent thin film which uses water, a solvent, a hydrolysis catalyst, a silicon alkoxide, and a fluorine content alkoxide as a start chemical, and is characterized by producing a firm water-repellent thin film on a substrate with a sol-gel method.
[Claim 2] As a silicon alkoxide One sort, such as the tetramethoxy silane (OCH3) Si 4, the tetra-ethoxy silane (OC2H5) Si 4, tetra-isopropoxysilane (OC3H9) Si 4, and tetra-normal butoxysilane (OC3H7) Si 4, or two sorts or more are used. It is a method of producing the water-repellent thin film according to claim 1 characterized by using CF3(CF2) nCH2-CH2SiCl3 (5 n= 0, 7) or CF3(CF2) nCH2-CH2Si (OCH3)3 (5 n= 0, 7) as a fluorine content alkoxide.
[Claim 3] 2-butanol, ethylene glycol, water, and a hydrochloric acid are put into a predetermined container. Ethyl orthosilicate is put in little by little, making it homogeneity and making [stir at a room temperature,] this solution stir. Fluoro silicon is put in little by little, stirring at a room temperature for 1 hour, and making a solution stir next. The method of producing the water-repellent thin film according to claim 1 which stirs at a room temperature for 1 hour, is made to carry out standing of this for one day, considers as a coating solution, and is characterized by dipping and pulling up a substrate in this solution, holding at 100 degrees C, heat-treating over 10 minutes - 60 minutes after that at 400 degrees C which is burning temperature, and producing a thin film.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the method of producing a water-repellent thin film, especially the fluorine content SiO2 water-repellence thin film by the sol-gel method.
[0002]
[Description of the Prior Art] DIPU coating is usually used for producing the coating film with a sol-gel method. By using the solution containing the compound of a metal alkoxide or others, although the uniform coating film can be easily produced over the whole substrate and a mechanical functional characteristic like a chemical protection, optical property, and electromagnetism property and a catalyst property is given, it is very useful. If it sees about the chemical protection-feature coating film, in order to raise the oxidation resistance of the metal substrate like a melting aluminum coat steel plate, and corrosion resistance in this, for example, A small amount of fluoro alkyl silane is added in the n-BuOH solution of an octylic acid zirconium. A thin film is produced by heat treatment. There is a report that 105 contact angles with water were acquired (). [K] . Izumi, H.Tanaka, M.Murakami, T.Deguchi, A.Morita, N.Tohgo and T, Minami, Abst, 5th Intnl.Sol-Gel Workshop:RiodeJaneiro, Brazil, 1989 Lecture number D 3-6. This report is producing the thin film using a zirconia system chemical from a viewpoint of oxidation resistance, and the substrate is restricted to the metal.
[0003]
[Problem(s) to be Solved by the Invention] In the above-mentioned report, the zirconia system chemical is used as the start raw material from a viewpoint of oxidation resistance and corrosion resistance, and the substrate is restricted to the metal. If such technique is applied to a glass substrate, the transparent and colorless film will be hard to be obtained from the relation of the refractive index of a zirconia, and it is known that endurance is inferior compared with the transparent and colorless film of a silica. This invention aims at producing a transparent and colorless and firm water-repellent thin film (contact angle 110 with water more than whenever) on various substrates, such as glass, plastics, and a metal. This invention is applicable to the glass with which water repellence and antifouling property are demanded, such as for example, glass for automobiles, a reflector glass, and a building, structural glass, ophthalmic glass, a plastic lens, etc.
[0004]
[Means for Solving the Problem] Since the above-mentioned purpose is attained, this invention can produce the thin film which uses hydrolysis catalysts, such as water, a solvent, and a hydrochloric acid, a silicon alkoxide, and a fluorine content alkoxide as a start chemical, is characterized by producing a firm water-repellent thin film on a substrate with a sol-gel method, and has the firm endurance which has fluorine association, and water repellence in the front face of SiO2.
[0005] In this invention as a silicon alkoxide One sort, such as the tetramethoxy silane (OCH3) Si 4, the tetra-ethoxy silane (OC2H5) Si 4, tetra-isopropoxysilane (iso-OC3H9) Si 4, and tetra-normal butoxysilane (n-OC3H7) Si 4, or two sorts or more can be used. As a fluorine content alkoxide, CF3 (CF2) nCH2-CH2SiCl3 (5 n= 0, 7) or CF3(CF2) nCH2-CH2Si (OCH3)3 (5 n= 0, 7) can be used. As a

solvent, a methanol, ethanol, ethylene glycol, a butanol (four sorts of isomers are included), propanol (two sorts of isomers are included), an acetone, etc. can be used. Various kinds of acids are used as a hydrolysis catalyst.

[0006] As the membrane formation approach, a dip method, a spin coat method, an ultrasonic spray method, etc. are applicable. Burning temperature for forming the coating film is made into 400 degrees C or less. Although temperature setups change with combination of a start chemical, when tetra-ethoxy silane, water, hydrochloric-acid, ethylene glycol, and CF3(CF2) nCH2-CH2SiCl3 is used when measured by TG (thermogravimetric measurement method) of desiccation gel, and DTA (differential-thermal-analysis method) for example, it holds at 100 degrees C and 400 degrees C is considered as multistage story baking of less than 1 hour.

[0007]

[Example 1] 15 mols of 2-butanol, one mol of ethylene glycol, ten mols of pure water, and 0.03 mols of hydrochloric acids are put into a propylene beaker, and it stirs at a room temperature, and is made homogeneity. One mol of tetra-ethoxy silanes was put in little by little, making this solution stir, and it stirred at the room temperature for 1 hour. Next, 0.05 mols (CF3(CF2)7CH2-CH2SiCl3) of fluoro silicon were put in little by little, making a solution stir, and it stirred at the room temperature for 1 hour. After carried out standing of this on the 1st, having considered as the coating solution, having dipped and pulled up various substrates (glass, metal) in this solution, holding by maintenance at 100 degrees C for 1 hour and holding at maintenance and 200 degrees C by 160 degrees C for 1 hour for 10 minutes, it heat-treated over 10 minutes - 60 minutes to 400 degrees C which is burning temperature, and the thin film was produced.

[0008] The following durability test was performed about the produced thin film.

1. Boiling test Ebullition underwater immersion Warm water-proof [5-hour 2.] trial 50-degree-C warm water immersion 240-hour 3. humidity resistance test 60 degrees C More than 95%RH 800-hour 4. direct weathering test It is left at a level with the outdoors. With no one-year or more change.
5. Ultraviolet-Rays Exposure Test A 63-degree-C (BP temperature) sunshine weather meter 1000-hour 6. antifriction trial The 300g/cm load 2, and 40 round trips / part (cotton flannel cloth of No. 300) 4000 round-trip 7. antifriction trial Although the pyrolysis of C-F association will happen and a contact angle will fall remarkably above 400 degrees C as drawing 1 if the 2000 flannel cloth round trip containing the glass cleaner liquid for automobiles, in addition the burning-temperature dependency of a contact angle are shown In baking to 400 degrees C, the thin film of 110 degrees of contact angles was obtained, and it was almost the same as 110 degrees of contact angles with early water. Moreover, as compared with the water-repellent thin film known conventionally, the thin film obtained by this invention had marked endurance.

[0009] When preparing the above-mentioned coating solution, it is uniform and the conditions of that the whole solution is uniform in order to produce the coating thin film which there is no crack and was strongly combined with the substrate, and existing [Si-OC2H5 in ethyl orthosilicate, such as a tetra-ethoxy silane, hydrolyze in a solution, and / sufficient Si-OH] ** are required. The sake, If ethyl orthosilicate is put in at a time, hydrolysis will advance partially and the uniform film will not be obtained. Similarly, fluoro silicon is put in little by little and it fully stirs, and the whole is uniform, makes, will carry out standing for one day, and will advance hydrolysis. The film that the coating solution immediately after stirring has inadequate hydrolysis and uniform was not attached. In this example, although the mixed solvent of 2-butanol and ethylene glycol is used, by evaporating a solvent little by little, this is uniform and is for making the film with a smooth front face while it gives a certain amount of viscosity to a solution and improves with the film by using a high-boiling point solvent.

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